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Magnetic and electric properties of stoichiometric $BiMnO_3$ thin films

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Abstract

It has been suggested that $BiMnO_3$ is a material exhibiting both ferromagnetism and ferroelectricity. Stoichiometry is rather easily achieved in a polycrystalline sample, and ferromagnetic properties have been well documented for bulk samples. Stoichiometry in thin films has been difficult to obtain, and many physical properties have exhibit wide distributions mainly due to the stoichiometry problem. Thin film studies on $BiMnO_3$ have not shown clear evidence of ferroelectricity, while other physical properties measured for the $BiMnO_3$ films showed wide spectra, which has been attributed to cation and/or oxygen vacancies. We fabricated $BiMnO_3$ thin films with good stoichiometry and with ferromagnetic properties comparable to those reported for stoichiometric $BiMnO_3$: $Tc \sim 105$ K and $M_{sat} \sim 3.6$ μ_B/Mn. The charge-electric field (Q-E) curve measured at 5 K was fairly linear and free from hysteresis and showed no ferroelectric order. This finding is consistent with the centrosymmetric crystal structure recently suggested by theoretical calculations and structural studies on ceramic samples of stoichiometric $BiMnO_3$.

Keywords: $BiMnO_3$; Multiferroic; Ferroelectric; Stoichiometric; Centrosymmetric

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Background

$BiMnO_3$ has received huge interest due to the possibility of coexistence of ferroelectricity and ferromagnetism [1-11]. $BiMnO_3$ has monoclinic symmetry with lattice parameters $a = 9.533$ Å, $b = 5.606$ Å, $c = 9.854$ Å, and $\beta = 110.667°$. The ferromagnetism has been explained in terms of orbital ordering of Mn^{4+} ions, while the Bi-6s lone pair was expected to result in ferroelectricity. The existence of ferromagnetism has been confirmed for both stoichiometric and ceramic $BiMnO_3$. Most studies of ceramic $BiMnO_3$ showed around the same ferromagnetic transition temperature of approximately 105 K, with a saturated magnetic moment of 3.6 μ_B/Mn, consistent with the high spin configuration of the Mn^{4+} ion. However, ferroelectricity of ceramic samples has not been measured. A sizable single crystal has not been obtained, and most measurements have been performed on polycrystalline samples requiring high-pressure synthesis.

It has been very difficult to obtain good stoichiometry in thin film $BiMnO_3$, and the physical properties measured for thin films of $BiMnO_3$ having unsatisfactory stoichiometry are often widely distributed. Thin film studies on $BiMnO_3$ have not detected ferroelectricity very clearly, while other physical properties measured for the films varied across a wide spectrum. The films also exhibited non-optimum magnetic properties. Ferromagnetic transition temperatures and saturated magnetic moments were smaller than those reported for stoichiometric ceramic $BiMnO_3$; thus, multiferroicity has not yet been accurately ascertained for *stoichiometric* $BiMnO_3$.

The first thin film of $BiMnO_3$ on $SrTiO_3$ (001) substrate had $Tc \sim 105$ K, and an x-ray diffraction rocking curve peak had full width at half maximum of approximately 1.1° [12]. In that study, no measurement was made of saturated magnetic moment, M_{sat}, and the existence of ferroelectricity was not confirmed. Son et al. reported writing polarization bits on $BiMnO_3$ thin films with a low Tc of approximately 50 K and full width at half maximum of approximately 0.4° [13]. $Pt/SrTiO_3/BiMnO_3/SrTiO_3/Pt$ and $SrRuO_3/SrTiO_3/BiMnO_3/SrTiO_3/SrRuO_3$ capacitors were also reported to show good ferroelectric properties with a remnant polarization of around 9 to 16 $\mu C/cm^2$ but in combination with a very small saturated magnetic moment, $M_{sat} < 1.0$ μ_B/Mn [14]. It is notable that ferroelectricity was reported to

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arise from $SrTiO_3$ itself [15-17]. A clear polarization electric field hysteresis curve was observed for a $BiMnO_3$/$SrTiO_3$ (001) structure grown using pulsed laser deposition with a high Bi-rich target of $Bi_{2.4}MnO_3$ [18]. However, the ferromagnetic properties of the film were not optimum: $Tc \sim 85$ K, $M_{sat} \sim 1$ μ_B/Mn. Ferromagnetic properties measured for $BiMnO_3$ films made using chemical solution deposition or rf-magnetron sputtering were less favorable compared to those of stoichiometric ceramic $BiMnO_3$ [19,20]. The depression in Curie temperature can be attributed to a non-stoichiometric composition, to strain, or to size effects [1].

Overall, the growth of $BiMnO_3$ thin films with correct stoichiometry, free from vacancies, and with ferromagnetic properties similar to those measured in bulk samples has not yet been reported. Thin film growth of $BiMnO_3$ suffers from high Bi volatility. To study the pertinent problem of multiferroicity in $BiMnO_3$, we fabricated thin films of $BiMnO_3$ with magnetic properties and stoichiometry matching those reported for high-pressure fabricated *stoichiometric* $BiMnO_3$. Using these films, we investigated the existence of ferroelectricity in stoichiometric $BiMnO_3$.

Methods

We fabricated $BiMnO_3$ thin films on a $SrTiO_3$ (001) substrate using a pulsed laser deposition method [21-24]. A KrF excimer laser with repetition rate of 4 Hz was used, and the optimum growth temperature was found to be very narrow: around approximately 500°C with oxygen partial pressure of approximately 10 mTorr. We used a freshly ground surface of $Bi_{1.2}MnO_3$ as the target. Note that the Bi overstoichiometry is rather small; together with the precise growth conditions, these characteristics of the target are one reason for the wide spectrum of physical properties reported in films. The number of pulses required per monolayer of $BiMnO_3$ was about 13.6. The thickness was estimated to be around $t \sim 88$ nm, using field emission scanning electron microscope. We performed a detailed x-ray diffraction study of the epitaxial structure of the $BiMnO_3$ films using high-resolution x-ray diffraction. For electrical transport studies, we used a physical property measurement system (Quantum Design, PPMS, San Diego, USA). Magnetic properties were determined using a superconducting quantum interference device (Quantum Design, MPMS, San Diego, USA). Ferroelectric characterization measurement with capacitance geometry was done on Nb-doped $SrTiO_3$ substrate\$BiMnO_3$\Au sample using a cryogenic probe station (Lake Shore Cryotronics, Inc., Westerville, USA) and semiconductor parameter analyzer (Agilent Technologies, Santa Clara, USA). The area of Au top electrode was approximately 100 μm × 100 μm.

Results and discussion

Figure 1a shows the $\theta - 2\theta$ patterns of the $BiMnO_3$/$SrTiO_3$ (001) structure. The (010) and (020) $BiMnO_3$ reflection peaks are clearly visible to the left of the $SrTiO_3$ substrate peaks. The calculated out-of-plane lattice constant for $BiMnO_3$ film peaks was 3.985 Å. No other Bragg diffraction peaks were observed for the films. The x-ray rocking curve of the (010) $BiMnO_3$ peak revealed a full width at half maximum as small as approximately 0.067°, lower than the 0.4° and 1.1° reported in previous studies [12,13].

The reciprocal space maps shown in Figure 1b confirm nearly coherent growth of a $BiMnO_3$ film on an $SrTiO_3$ (001) substrate with an in-plane lattice constant of 3.909 Å. The calculated volume of one unit cell of $BiMnO_3$ ($V_{film} = 60.89$ Å^3) in the film was 98.9% that of bulk monoclinic $BiMnO_3$ ($V_{bulk} = 61.58$ Å^3). The roughly 1% volume reduction is mostly due to compressive strain from the $SrTiO_3$ substrate. The slightly smaller unit cell volume measured for the film demonstrates that our *stoichiometric* $BiMnO_3$ has negligible cation or oxygen vacancies.

The ferromagnetic properties for our *stoichiometric* $BiMnO_3$ films were investigated, to compare their performance with that reported for stoichiometric ceramic bulk $BiMnO_3$. Figure 2a shows the temperature dependence of magnetization at 1 T after 7 T field cooling. We measured a Tc of 105 K, close to that of the stoichiometric $BiMnO_3$ bulk sample. Figure 2b shows magnetic hysteresis (M-H) curves at 5 K. The saturated magnetic moment is as high as 3.8 μ_B/Mn, close to that reported for stoichiometric $BiMnO_3$ bulk. The magnetic coercive field was approximately 700 Oe, which is slightly larger than that measured for other manganese perovskite oxides such as (La,Ca,Sr)MnO_3, and about two orders of magnitude smaller than that reported for $SrRuO_3$ [24,25]. For ferromagnetic perovskite oxides, a larger epitaxial strain usually results in enhancement of magnetic coercive field and the lattice mismatch of $BiMnO_3$ with respect to the $SrTiO_3$ substrate is larger than the lattice mismatch of (La,Ca,Sr)MnO_3 with respect to the commonly used of $SrTiO_3$ substrate.

After confirming good stoichiometry and ferromagnetic properties, comparable to those of *stoichiometric* bulk $BiMnO_3$, we investigated the existence of multiferroicity in our $BiMnO_3$ films. First, in-plane resistivity was measured, as shown in Figure 3a. The resistivity of the film shows semiconducting behavior with $\rho(T = 300\text{ K}) \sim 4 \times 10^4$ $\Omega\cdot$cm and $\rho(T = 100\text{ K}) \sim 10^{11}$ $\Omega\cdot$cm. This room temperature resistivity is larger than the room temperature values of 2×10^4 $\Omega\cdot$cm measured for polycrystalline ceramics [5] and 1.8×10^2 $\Omega\cdot$cm reported for epitaxial films [26]. However, this value is much smaller than the 5×10^7 $\Omega\cdot$cm measured for a '*highly resistive film*' [27]. It is notable that

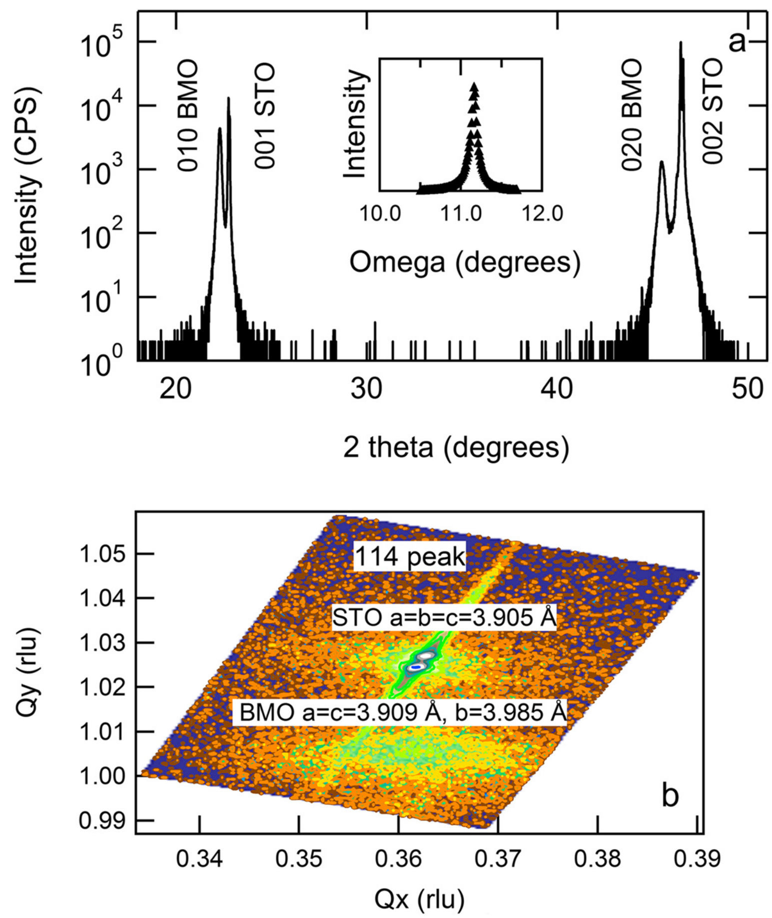

Figure 1 The $\theta - 2\theta$ patterns of the $BiMnO_3/SrTiO_3$ (001) structure and the reciprocal space maps. (a) XRD $\theta - 2\theta$ patterns for the $BiMnO_3/SrTiO_3$ (001) heterostructure. Inset shows the rocking curve for a (010) $BiMnO_3$ peak. The x-ray rocking curve of the (010) $BiMnO_3$ peak revealed a full width at half maximum as small as approximately 0.067°. **(b)** X-ray reciprocal space mapping around the $SrTiO_3$ (114) plane shows well-developed peaks for $BiMnO_3$ in the lower region and two strong substrate peaks in the upper region.

the out-of-plane lattice parameter of 4.004 Å reported for the '*highly resistive film*' is significantly larger than our value of 3.985 Å, and that the saturated magnetic moment of 2.0 μ_B/Mn for the '*highly resistive film*' is much smaller than our value of 3.8 μ_B/Mn. Usually, a larger unit cell volume in perovskite-based metal oxides arises from cation or oxygen vacancies, which dramatically change transport properties more than magnetic properties [28]. Gajek *et al.* demonstrated spin filtering in the $BiMnO_3$ junction [26] and observed that significant changes of unit cell volume measured in films arise from Bi vacancies that locally disturb the complex orbital ordering essential for long-range ferromagnetic order in $BiMnO_3$. A change of unit cell volume was accompanied by small room temperature resistivity values and lower saturated magnetic moment in the magnetic hysteresis curve [26].

Finally, we measured the charge-electric field (Q-E) curve to obtain evidence of ferroelectricity in the *stoichiometric* $BiMnO_3$ film. Figure 3b shows Q-E curves at 5 K, where leakage problems, as shown in Figure 3a, do not occur. The Q-E curve measured at 5 K was fairly linear and free from hysteresis, and no ferroelectric order was observed. The absence of ferroelectric order in our *stoichiometric* film seems to be strengthened by the observation that the unit cell volume supports stoichiometry, that crystallinity is excellent, and ferromagnetic properties are as good as those reported for *stoichiometric* $BiMnO_3$ samples.

Recently, there has been doubt about observations of ferroelectricity in some $BiMnO_3$ films. It was reported theoretically that the ground state for $BiMnO_3$ either with or without strain should be a centrosymmetric structure [29,30]. Rigorous structural studies on ceramic samples using transmission electron microscope and neutron diffraction data showed that $BiMnO_3$ crystallizes in the centrosymmetric space group C2/c at 300 K [31]. It was suggested that the weak ferroelectric polarizations measured on $BiMnO_3$ samples originated from an ordered oxygen deficiency [32].

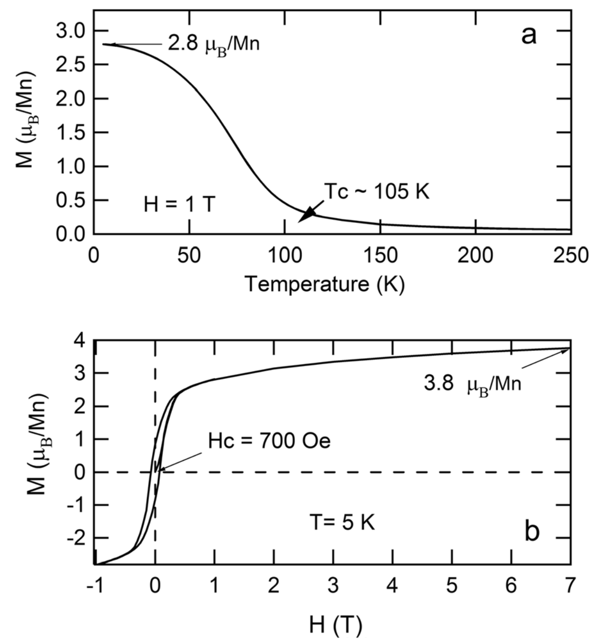

Figure 2 Magnetization curves and magnetic hysteresis curves for $BiMnO_3/SrTiO_3$ (001) structure. (a) Magnetization curves for $BiMnO_3/SrTiO_3$ (001) structure at 1 T after 7-T high field cooling. **(b)** Magnetic hysteresis curves for $BiMnO_3/SrTiO_3$ (001) structure at 5 K.

Conclusions

In summary, we investigated the existence of ferroelectricity in *stoichiometric* $BiMnO_3$. We produced high-quality thin films with good stoichiometry and with magnetic properties - such as *Tc* and saturated magnetic moment - comparable to those reported for bulk *stoichiometric* $BiMnO_3$. The structural quality was evidenced by narrow full width at half maximum for XRD peaks and good reciprocal space mapping data. Since vacancies in perovskite oxide film affect transport properties more than ferromagnetic properties, we believe that our *stoichiometric* $BiMnO_3$ films should have sufficient quality for ascertaining the existence of ferroelectricity in *stoichiometric* $BiMnO_3$. We found that the resistivity of the film demonstrates semiconducting behavior, with $\rho(T = 300\ \text{K}) \sim 4 \times 10^4\ \Omega{\cdot}\text{cm}$. The Q-E curve measured at 5 K was fairly linear and free from hysteresis, and no ferroelectric order was observed. This finding is consistent with the centrosymmetric crystal structure recently suggested by theoretical calculations and structural studies on ceramic samples of *stoichiometric* $BiMnO_3$. If ferroelectricity does exist in both stoichiometric $BiMnO_3$ and non-stoichiometric $BiMnO_3$, then Bi-6s lone pair scenario should be the best answer for the origin. Summarizing our work and other works, the existence of ferroelectricity seems to depend on the stoichiometry very sensitively. Then, other origin should be considered at least together since Bi-6s lone pair exists both for stoichiometric $BiMnO_3$ without showing FE and non-stoichiomeric $BiMnO_3$ showing FE.

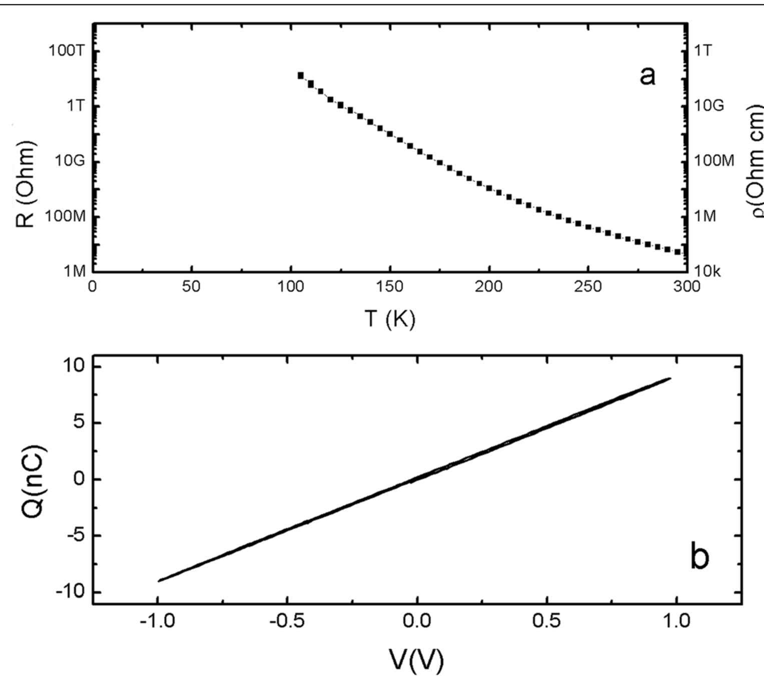

Figure 3 Temperature dependence of resistivity and charge-electric field (Q-E) curve for $BiMnO_3/SrTiO_3$ (001) structure. (a) Temperature dependence of resistivity for $BiMnO_3/SrTiO_3$ (001) structure. **(b)** Charge-electric field (Q-E) curves for $BiMnO_3/SrTiO_3$ (001) structure at 5 K.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
PSY, VBN, and KRNT contributed to the introduction of key concept. CUJ did the whole experiments and organized the manuscript as the corresponding author. BWL motivated the work and joined the discussion. All authors read and approved the final manuscript.

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